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Invention: FLASH MEMORY DEVICE AND A FABRICATION PROCESS THEREOF, METHOD OF FORMING A DIELECTRIC FILM

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☐ Regular Utility Application

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SPECIFICATION

VERIFICATION OF TRANSLATION

I, Tadahiko Itoh, a Patent Attorney of Tokyo, Japan having my office at 32nd Floor, Yebisu Garden Place Tower, 20-3 Ebisu 4-Chome, Shibuya-Ku, Tokyo 150-6032, Japan, am the translator of the documents attached and I state that the following is a true English translation to the best of my knowledge and belief of United States Patent Application **filed May 31, 2001**, **Attorney's Docket No.GJP/M281230/OHMI** in the Japanese language.

DATED this 23rd day of July, 2001

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DESCRIPTION

<u>FLASH MEMORY DEVICE AND FABRICATION PROCESS THEREOF,</u>

<u>METHOD OF FORMING A DIELECTRIC FILM</u>

5 <u>TECHNICAL FIELD</u>

The present invention generally relates to
semiconductor devices and a fabrication process
thereof. More particularly, the present invention
relates to a method of forming a dielectric film and
10 fabrication process of a non-volatile semiconductor
memory device capable of rewriting information
electrically, including a flash memory device.

There are various volatile memory devices
such as DRAMs and SRAMs. Further, there are non-
15 volatile memory devices such as a mask ROM, PROM,
EPROM, EEPROM, and the like. Particularly, a flash
memory device is an EEPROM having a single transistor
for one memory cell and has an advantageous feature
of small cell size, large storage capacity and low
20 power consumption. Thus, intensive efforts are being
made on the improvement of flash memory devices. In
order that a flash memory device can be used stably
over a long interval of time with low voltage, it is
essential to use a uniform insulation film having
25 high film quality.

<u>BACKGROUND ART</u>

First, the construction of a conventional
flash memory device will be explained with reference
30 to FIG.1 showing the concept of a generally used
flash memory device having a so-called stacked gate
structure.

Referring to FIG.1, the flash memory device

is constructed on a silicon substrate 1700 and includes a source region 1701 and a drain region 1702 formed in the silicon substrate 1700, a tunneling gate oxide film 1703 formed on the silicon substrate 1700 between the source region 1701 and the drain region 1702, and a floating gate 1704 formed on the tunneling gate oxide film 1703, wherein there is formed a consecutive stacking of a silicon oxide film 1705, a silicon nitride film 1706 and a silicon oxide film 1707 on the floating gate 1704, and a control gate 1708 is formed further on the silicon oxide film 1707. Thus, the flash memory of such a stacked structure includes a stacked structure in which the floating gate 1704 and the control gate 1708 sandwich an insulating structure formed of the insulation films 1705, 1706 and 1707 therebetween.

The insulating structure provided between the floating gate 1704 and the control gate 1705 is generally formed to have a so-called ONO structure in which the nitride film 1706 is sandwiched by the oxide films 1705 and 1707 for suppressing the leakage current between the floating gate 1704 and the control gate 1705. In an ordinary flash memory device, the tunneling gate oxide film 1703 and the silicon oxide film 1705 are formed by a thermal oxidation process, while the silicon nitride film 1706 and the silicon oxide film 1707 are formed by a CVD process. The silicon oxide film 1705 may be formed by a CVD process. The tunneling gate oxide film 1703 has a thickness of about 8nm, while the insulation films 1705, 1706 and 1707 are formed to have a total thickness of about 15 nm in terms of oxide equivalent thickness. Further, a low-voltage transistor having a

gate oxide film of 3 - 7 nm in thickness and a high-voltage transistor having a gate oxide film of 15 - 30 nm in thickness are formed on the same silicon in addition to the foregoing memory cell.

In the flash memory cell having such a stacked structure, a voltage of about 5 - 7V is applied for example to the drain 1702 when writing information together with a high voltage larger than 12V applied to the control gate 1708. By doing so, the channel hot electrons formed in the vicinity of the drain region 1702 are accumulated in the floating gate via the tunneling insulation film 1703. When erasing the electrons thus accumulated, the drain region 1702 is made floating and the control gate 1708 is grounded. Further, a high voltage larger than 12V is applied to the source region 1701 for pulling out the electrons accumulated in the floating gate 1704 to the source region 1701.

Such a conventional flash memory device, on the other hand, requires a high voltage at the time of writing or erasing of information, while the use of such a high voltage tends to cause a large substrate current. The large substrate current, in turn, causes the problem of deterioration of the tunneling insulation film and hence the degradation of device performance. Further, the use of such a high voltage limits the number of times rewriting of information can be made in a flash memory device and also causes the problem of erroneous erasing.

The reason a high voltage has been needed in conventional flash memory devices is that the ONO film, formed of the insulation films 1705, 1706 and 1707, has a large thickness.

In the conventional art of film formation, there has been a problem, when a high-temperature process such as thermal oxidation process is used in the process of forming an oxide film such as the

5 insulation film 1705 on the floating gate 1704, in that the quality of the interface between the polysilicon gate 1704 and the oxide film tends to become poor due to the thermal budget effect, etc. In order to avoid this problem, one may use a low

10 temperature process such as CVD process for forming the oxide film. However, it has been difficult to form a high-quality oxide film according to such a low-temperature process. Because of this reason, conventional flash memory devices had to use a large

15 thickness for the insulation films 1705, 1706 and 1707 so as to suppress the leakage current.

However, the use of large thickness for the insulation films 1705, 1706 and 1707 in these conventional flash memory devices has caused the

20 problem in that it is necessary to use a large writing voltage and also a large erasing voltage. As a result of using large writing voltage and large erasing voltage, it has been necessary to form the tunneling gate insulation film 1703 with large

25 thickness so as to endure the large voltage used.

DISCLOSURE OF THE INVENTION

Accordingly, it is a general object of the present invention to provide a novel and useful flash

30 memory device and fabrication process thereof and further a method of forming an insulation film, wherein the foregoing problems are eliminated.

Another and more specific object of the

present invention is to provide a high-performance flash memory device having a high-quality insulation film that is formed at a low temperature process, the thickness of the tunneling gate insulation film or

5 the thickness of the insulation film between the floating gate and the control gate can be reduced successfully without causing the problem of leakage current, and enabling writing and erasing at low voltage.

10 Another object of the present invention is to provide a method of forming an insulation film wherein a high-quality insulation film can be formed on polysilicon.

Another object of the present invention is

15 to provide a flash memory device, comprising:

a silicon substrate,

a first electrode formed on the silicon substrate with a tunneling insulation film interposed therebetween, and

20 a second electrode formed on the first electrode with an insulation film interposed therebetween,

said insulation film having a stacked structure including at least one silicon oxide film

25 and one silicon nitride film, at least a part of said silicon oxide film containing Kr with a surface density of $10^{10} cm^{-2}$ or more.

According to the present invention, the quality of the insulation film used in a flash memory

30 device between a floating gate electrode and a control gate electrode is improved by forming the insulation film by an oxidation reaction or nitriding reaction conducted in Ar or Kr plasma in which atomic

state oxygen O* or hydrogen nitride radicals NH* are formed efficiently. Further, it becomes possible to reduce the thickness of the insulation film without causing unwanted increase of leakage current. As a result, the flash memory device of the present invention can operate at high speed with low voltage and has a long lifetime.

Another object of the present invention is to provide a method of fabricating a flash memory device comprising a silicon substrate, a first electrode of polysilicon formed on the silicon substrate with an insulation film interposed therebetween, and a second electrode formed on the first electrode with an inter-electrode insulation film interposed therebetween, said inter-electrode insulation film having a stacked structure containing at least one silicon oxide film and one silicon nitride film,

said silicon oxide film being formed by the step of exposing a silicon oxide film deposited by a CVD process to atomic state oxygen O* formed by microwave excitation of plasma in a mixed gas of an oxygen-containing gas and an inert gas predominantly of a Kr gas.

According to the present invention, an oxide film having excellent leakage current characteristic is obtained for the inter-electrode insulation film, and it becomes possible to form a flash memory having a simple structure, capable of holding electric charges in the floating gate electrode stably, and is operable at a low driving voltage.

Another object of the present invention is

to provide a fabrication process of a flash memory device comprising a silicon substrate, a first electrode of polysilicon formed on the silicon substrate with an insulation film interposed

5 therebetween, and a second electrode formed on the first electrode with an inter-electrode insulation film interposed therebetween, said inter-electrode insulation film having a stacked structure including at least one silicon oxide film and one silicon

10 nitride film,

said silicon nitride film being formed by exposing a silicon nitride film deposited by a CVD process to hydrogen nitride radicals NH* formed by microwave excitation of plasma in a mixed gas of an

15 NH$_3$ gas or alternatively a gas containing N$_2$ and H$_2$ and a gas predominantly formed of an Ar or Kr gas.

According to the present invention, a nitride film having excellent leakage current characteristic suitable for the inter-electrode

20 insulation film is obtained. Thus, it becomes possible to realize a flash memory having a simple construction and is capable of holding electric charges stably in the floating gate electrode. The flash memory thus obtained is operable at a low

25 driving voltage.

Another object of the present invention is to provide a method of forming a silicon oxide film, comprising the steps of:

depositing a polysilicon film on a

30 substrate; and

forming a silicon oxide film on a surface of said polysilicon film by exposing the surface of said polysilicon film to atomic state oxygen O*

formed by microwave excitation of plasma in a mixed gas of a gas containing oxygen and an inert gas predominantly of a Kr gas.

According to the present invention, it becomes possible to form a homogeneous silicon oxide film on a polysilicon film with uniform thickness irrespective of the orientation of the silicon crystals therein. The silicon oxide film thus formed has excellent leakage current characteristic comparative to that of a thermal oxide film and causes a Fowler-Nordheim tunneling similarly to the case of a thermal oxide film.

Another object of the present invention is to provide a method of forming a silicon nitride film, comprising the steps of:

depositing a polysilicon film on a substrate; and

forming a nitride film on a surface of said polysilicon film by exposing the surface of said polysilicon film to hydrogen nitride radicals NH* formed by microwave excitation of plasma in a mixed gas of a gas containing nitrogen and hydrogen as constituent elements and an inert gas predominantly of an Ar gas or a Kr gas.

According to the present invention, it becomes possible to form a nitride film of excellent characteristic on the surface of a polysilicon film.

Another object of the present invention is to provide a method of forming a dielectric film, comprising the steps of:

depositing a polysilicon film on a substrate; and

converting a surface of said polysilicon

film into a dielectric film by exposing said
polysilicon film to a microwave-excited plasma formed
in a mixed gas of an inert gas predominantly of Ar or
Kr and a gas containing oxygen as a constituent

5 element and a gas containing nitrogen as a
constituent element.

According to the present invention, it
becomes possible to form an oxynitride film having
excellent characteristic on the surface of a

10 polysilicon film.

Another object of the present invention is
to provide a method of fabricating a flash memory
having a silicon substrate, a first electrode of
polysilicon formed on said silicon substrate with an

15 insulation film interposed therebetween, and a second
electrode formed on said first electrode with an
inter-electrode oxide film interposed therebetween,
said inter-electrode oxide film being formed by the
steps of:

20 depositing a polysilicon film on said
silicon substrate as said first electrode; and

exposing a surface of said polysilicon film
to atomic state oxygen O* formed by microwave
excitation of plasma in a mixed gas of a gas

25 containing oxygen and an inert gas predominantly of a
Kr gas.

According to the present invention, an
oxide film having excellent leakage current
characteristic is obtained for the inter-electrode

30 insulation film, and it becomes possible to realize a
flash memory having a simple construction and is
capable of holding electric charges in the floating
gate electrode stably. The flash memory thus formed

is operable at a low driving voltage.

Another object of the present invention is to provide a method of fabricating a flash memory having a silicon substrate, a first electrode of polysilicon formed on said silicon substrate with an oxide film interposed therebetween, and a second electrode of polysilicon formed on said first electrode with an inter-electrode nitride film interposed therebetween, said inter-electrode nitride film being formed by the steps of:

depositing a polysilicon film on said silicon substrate as said first electrode; and

exposing a surface of said polysilicon film to hydrogen nitride radicals NH* formed by microwave excitation of plasma in a mixed gas of a gas containing nitrogen and hydrogen and an inert gas predominantly of an Ar gas or a Kr gas.

According to the present invention, a nitride film having excellent leakage current characteristic is obtained for the inter-electrode nitride film and it becomes possible to realize a flash memory having a simple construction and is capable of holding electric charges in the floating gate electrode stably. The flash memory thus formed is operable at a low driving voltage.

Another object of the present invention is to provide a method of fabricating a flash memory having a silicon substrate, a first electrode of polysilicon formed on said silicon substrate with insulation film interposed therebetween, and a second electrode of polysilicon formed on said first electrode with an inter-electrode oxynitride film interposed therebetween, said inter-electrode

oxynitride film being formed by the steps of:

depositing a polysilicon film on said
silicon substrate as said first electrode; and

converting a surface of said polysilicon
film into a silicon oxynitride film by exposing said
polysilicon film to microwave excited plasma formed
in a mixed gas of an inert gas predominantly of Ar or
Kr and a gas containing oxygen and nitrogen.

According to the present invention, an
oxynitride film having excellent leakage current
characteristic is obtained for the inter-electrode
insulation film, and it becomes possible to realize a
flash memory capable of holding electric charges
stably in the floating gate electrode. The flash
memory thus formed is operable at a low driving
voltage.

Another object of the present invention is
to provide a method of forming a silicon oxide film
on a polysilicon film, comprising the steps of:

forming atomic state oxygen O* in a
processing vessel of a microwave processing apparatus,
said microwave processing apparatus including: a
shower plate in a part of said processing vessel such
that said shower plate extends parallel to a
substrate to be processed, said shower plate having a
plurality of apertures for supplying a plasma gas
toward said substrate; and a microwave radiation
antenna emitting a microwave into said processing
vessel via said shower plate, by supplying a gas
predominantly of Kr and a gas containing oxygen into
said processing vessel via said shower plate and
further by supplying said microwave into said
processing vessel from said microwave radiation

antenna through said shower plate; and

forming a silicon oxide film by causing oxidation in a surface of a polysilicon film formed on said substrate by said plasma in said processing

5   vessel.

According to the present invention, atomic state oxygen that cause oxidation in a polysilicon film are formed efficiently by inducing high-density plasma of low electron temperature in the processing

10   chamber as a result of microwave excitation of the plasma gas supplied uniformly from the shower plate. The silicon oxide film thus formed by the Kr plasma is irrelevant to the crystal orientation of the Si crystals on which the silicon oxide film is formed.

15   Thus, the silicon oxide film is formed uniformly on the polysilicon film. The silicon oxide film contains little surface states and is characterized by small leakage current. According to the present invention, the oxidation processing of the polysilicon film can

20   be conducted at a low temperature of 550°C or less, and there occurs no substantial grain growth in the polysilicon film even when such an oxidation process is conducted. Thus, the problem of concentration of electric field, and the like, which arises with such

25   a grain growth is avoided.

Another object of the present invention is to provide a method of forming a silicon nitride film on a polysilicon film, said method comprising the steps of:

30   forming plasma containing hydrogen nitride radicals NH* in a processing vessel of a microwave processing apparatus, said microwave processing apparatus including: a shower plate in a part of said

processing vessel so as to extend parallel to a
substrate to be processed, said shower plate having a
plurality of apertures for supplying a plasma gas to
said substrate; and a microwave radiation antenna

5   emitting a microwave into said processing vessel via
said shower plate, by supplying a gas predominantly
of Ar or Kr and a gas containing nitrogen and
hydrogen into said processing vessel from said shower
plate and by further supplying said microwave into

10   said processing vessel from said microwave radiation
antenna through said shower plate; and

        forming a silicon nitride film by nitriding
a surface of a polysilicon film formed on said
substrate by said plasma in said processing vessel.

15   According to the present invention,
hydrogen nitride radicals NH* that cause nitridation
in the polysilicon film are formed efficiently by
inducing high-density plasma having a low electron
temperature in the processing chamber by microwave

20   excitation of the plasma gas supplied uniformly from
the shower plate. The silicon nitride film thus
formed by the Kr plasma has an advantageous feature
of small leakage current in spite of the fact that
the silicon nitride film is formed at a low

25   temperature.

        Another object of the present invention is
to provide a method of fabricating a flash memory
device, said flash memory device having a silicon
substrate and including a first electrode formed on

30   said silicon substrate with a tunneling insulation
film interposed therebetween and a second electrode
formed on said first electrode with an insulation
film interposed therebetween, said insulation film

having a stacked structure containing at least one silicon oxide film and one silicon nitride film, said silicon oxide film being formed by the steps of:

introducing a gas containing oxygen and a

5   gas predominantly of a Kr gas into a processing chamber, and causing microwave excitation of plasma in said processing chamber.

According to the present invention, it becomes possible to oxidize the surface of the first

10   electrode at low temperature, by conducting the oxidation processing in the Kr plasma in which atomic state oxygen O* are formed efficiently. As a result, an oxide film containing small surface states and is characterized by small leakage current can be

15   obtained for the desired silicon oxide film.

Another object of the present invention is to provide a fabrication process of a flash memory device having a silicon substrate, a first electrode formed on said silicon substrate with a tunneling

20   insulation film interposed therebetween, and a second electrode formed on said first electrode with an insulation film interposed therebetween, said insulation film having a stacked structure containing at least one silicon oxide film and one silicon

25   nitride film,

said silicon nitride film being formed by introducing an NH_3 gas or a gas containing N_2 and H_2 and a gas predominantly of Ar or Kr into a processing chamber, and causing microwave excitation of plasma

30   in said processing chamber.

According to the present invention, it becomes possible to nitride the surface of the first electrode at low temperature by conducting the

nitridation in the plasma of Ar or Kr in which the
hydrogen nitride radicals NH* are formed efficiently.

Other objects and further features of the
present invention will become apparent from the
following detailed description of the invention when
read in conjunction with the attached drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG.1 is a cross-sectional diagram showing
a schematic cross-section of a conventional flash
memory device;

FIG.2 is a diagram showing the concept of
the plasma apparatus that uses a radial line slot
antenna:

FIG.3 is a diagram showing the relationship
between a thickness and a gas pressure in a
processing chamber for an oxide film formed according
to a first embodiment of the present invention;

FIG.4 is a diagram showing the relationship
between the thickness and duration of oxidation for
the oxide film formed according to the first
embodiment of the present invention;

FIG.5 is a diagram showing the depth
profile of Kr density in the silicon oxide film
according to the first embodiment of the present
invention;

FIG.6 is a diagram showing the surface
state density in the silicon oxide film according to
the first embodiment of the present invention;

FIG.7 is a diagram showing the relationship
between the surface state density and the breakdown
voltage for the silicon oxide film according to the
first embodiment of the present invention;

FIGS.8A and 8B are diagrams showing the
relationship between the surface state density and
break down voltage of the silicon oxide film obtained
according to the first embodiment of the present
5   invention and the total pressure of the processing
chamber;

FIG.9 is a diagram showing the dependence
of film thickness on the total pressure used in the
processing chamber for a nitride film formed
10   according to a second embodiment of the present
invention;

FIG.10 is a diagram showing the current-
voltage characteristic of the silicon nitride film
according to the second embodiment of the present
15   invention;

FIGS.11A and 11B are diagrams showing the
oxidation process, nitriding process and oxy-
nitriding process of a polysilicon film according to
a third embodiment of the present invention;

20   FIG.12 is a diagram showing the dependence
of film thickness on the oxidation duration for an
oxide film obtained by an oxidation processing of a
polysilicon film according to a third embodiment of
the present invention;

25   FIGS.13A - 13C are diagrams showing a
change of surface morphology associated with the
oxidation process of a polysilicon film according to
the third embodiment of the present invention;

FIGS.14A and 14B are diagrams showing a
30   change of surface morphology of a polysilicon film
when subjected to a thermal oxidation process;

FIGS.15A and 15B are diagrams showing the
transmission electron microscope image of a

polysilicon film formed according to the third embodiment of the present invention;

FIGS.16 - 17 are diagrams showing the electric properties of the oxide film formed on a polysilicon according to the third embodiment of the present invention in comparison with a thermal oxide film;

FIG.18 is a diagram showing the cross-sectional structure of a flash memory device according to a fourth embodiment of the present invention;

FIG. 19 is a diagram showing the cross-sectional structure of a flash memory device according to a fifth embodiment of the present invention;

FIGS.20 - 23 are diagrams showing the fabrication process of a flash memory device according to a fifth embodiment of the present invention;

FIG.24 is a diagram showing the cross-sectional structure of the flash memory device according to a sixth embodiment of the present invention; and

FIG.25 is a diagram showing the cross-sectional structure of a flash memory device according to a seventh embodiment of the present invention.

BEST MODE FOR IMPLEMENTING THE INVENTION

Hereinafter, embodiments of the present invention will be described.

[FIRST EMBODIMENT]

First, low temperature oxide film formation using plasma will be described.

FIG.2 is a cross sectional diagram showing the construction of an exemplary microwave plasma processing apparatus used in the present invention for realizing the oxidation process, wherein the microwave plasma processing apparatus uses a radial line slot antenna (see WO98/33362). The novel feature of the present embodiment is to use Kr as the plasma excitation gas at the time of forming the oxide film.

Referring to FIG.2, the microwave plasma processing apparatus includes a vacuum vessel (processing chamber) 101 accommodating therein a stage 104 on which a substrate 103 to be processed is supported. The processing chamber 101 is evacuated to a vacuum state, and a Kr gas and an O_2 gas are introduced from a shower plate 102 formed at a part of the wall of the processing chamber 101 such the pressure inside the processing chamber is set to about 1 Torr (about 133 Pa). Further, a disk-shaped substrate such as a silicon wafer is placed on the stage 104 as the foregoing substrate 103. The stage 104 includes a heating mechanism, and the temperature of the substrate 103 is set to about 400°C. It is preferable to set the temperature in the range of 200 - 550°C. As long as the temperature is set in this range, a similar result is obtained.

Next, a microwave of 2.45 GHz is supplied from an external microwave source via a coaxial waveguide 105 connected thereto, wherein the microwave thus supplied is radiated into the processing chamber 101 by the radial line slot antenna 106 through a dielectric plate 107. As a

result, there is formed high-density plasma in the
processing chamber 101. As long as the frequency of
the microwave is in the range of 900 MHz or more but
not exceeding 10 GHz, a similar result is obtained as

5   described below. In the illustrated example, the
distance between the shower plate 102 and the
substrate 103 is set to about 6cm. Narrower the
distance, faster the film forming process.

       In the microwave plasma processing
10   apparatus of FIG.2, it becomes possible to realize a
plasma density exceeding $1 \times 10^{12} cm^{-3}$ at the surface
of the substrate 103. Further, the high-density
plasma thus formed by microwave excitation has a low
electron temperature, and a plasma potential of 10 V

15   or less is realized at the surface of the substrate
103. Thus, the problem of the substrate 103 being
damaged by the plasma is positively eliminated.
Further, there occurs no problem of contamination of
the substrate 103 because of the absence of plasma

20   sputtering in the processing chamber 101. Because of
the fact that the plasma processing is conducted in a
narrow space between the shower plate 102 and the
substrate 103, the product material of the reaction
flows quickly in the lateral direction to a large

25   volume space surrounding the stage 104 and is
evacuated. Thereby, a very uniform processing is
realized.

       In the high-density plasma in which an Kr
gas and an O_2 gas are mixed, Kr* at the intermediate
30   excitation state cause collision with the O_2
molecules and there occurs efficient formation of
atomic state oxygen O*, and the atomic state oxygen
O* thus formed cause oxidation of the substrate

surface. It should be noted that oxidation of a silicon surface has conventionally been conducted by using H_2O or O_2 molecules at very high process temperature such as 800°C or more. In the case of

5 using atomic state oxygen, on the other hand, it becomes possible to carry out the oxidation process at a low temperature of 550°C or less.

In order to increase the chance of collision between K* and O_2, it is preferable to

10 increase the pressure in the processing chamber 101. On the other hand, the use of too high pressure in the processing chamber increases the chance that O* causing collision with another O* and returning to the O_2 molecule. Thus, there would exist an optimum

15 gas pressure.

FIG.3 shows the thickness of the oxide film for the case in which the total pressure inside the processing chamber 101 is changed while maintaining the Kr and oxygen pressure ratio such that the

20 proportion of Kr is 97% and the proportion of oxygen is 3%. In the experiment of FIG.3, it should be noted that the silicon substrate was held at 400°C and the oxidation was conducted over the duration of 10 minutes.

25 Referring to FIG.3, it can be seen that the thickness of the oxide film becomes maximum when the total gas pressure in the processing chamber 101 is set to 1 Torr, indicating that the oxidation process becomes optimum under this pressure or in the

30 vicinity of this pressure. Further, it should be noted that this optimum pressure remains the same in the case the silicon substrate has the (100) oriented surface and also in the case the silicon substrate

has the (111) oriented surface.

FIG.4 shows the relationship between the thickness of the oxide film and the duration of the oxidation processing for the oxide film that is formed by oxidation of the silicon substrate surface using the Kr/O_2 high-density plasma. In FIG.4, the result for the case in which the silicon substrate has the (100) oriented surface and the result for the case in which the silicon substrate has the (111) oriented surface are both represented. Further, FIG.4 also represents the oxidation time dependence for the case a conventional dry oxidation process at the temperature of 900°C is employed.

Referring to FIG.4, it can be seen that the oxidation rate caused by the Kr/O_2 high-density plasma oxidation processing, conducted at the temperature of 400°C under the chamber pressure of 1 Torr, is larger than the oxidation rate for a dry O_2 process conducted at 900°C under the atmospheric pressure.

In the case of conventional dry thermal oxidation process at 900°C, it can be seen that the growth rate of the oxidation film is larger when the oxide film is formed on the (111) oriented silicon surface as compared with the case of forming the oxide film on the (100) oriented silicon surface. In the case in which the Kr/O_2 high-density plasma oxidation process is used, on the other hand, this relationship is reversed and the growth rate of the oxide film on the (111) surface is smaller than the growth rate of the oxide film on the (100) surface. In view of the fact that silicon atoms are arranged with larger surface density on the (111) oriented

surface than on the (100) oriented surface in a Si
substrate, it is predicted that the oxidation rate
should be smaller on the (111) surface than on the
(100) surface as long as the supply rate of the

5   oxygen radicals is the same. The result of the
foregoing oxidation process of the silicon substrate
surface is in good conformity with this prediction
when the Kr/O$_2$ high-density plasma is used for the
oxidation process, indicating that there is formed a

10   dense oxide film similar to the one formed on a (100)
surface, also on the (111) surface. In the
conventional case, on the other hand, the oxidation
rate of the (111) surface is much larger than the
oxidation rate of the (100) surface. This indicates

15   that the oxide film formed on the (111) film would be
sparse in quality as compared with the oxide film
formed on the (100) surface.

        FIG.5 shows the depth profile of the Kr
density inside the silicon oxide film that is formed

20   according to the foregoing process, wherein the depth
profile FIG.5 was obtained by a total-reflection
fluorescent X-ray spectrometer. In the experiment of
FIG.5, the formation of the silicon oxide film was
conducted at the substrate temperature of 400°C while

25   setting the oxygen partial pressure in the Kr gas to
3% and setting the pressure of the processing chamber
to 1 Torr (about 133 Pa).

        Referring to FIG.5, it can be seen that the
surface density of Kr decreases toward the

30   silicon/silicon oxide interface, and a density of 2 x
10^{11}cm^{-2} is observed at the surface of the silicon
oxide film. Thus, the result of FIG.5 indicates that
a substantially uniform Kr concentration is realized

in the silicon oxide film when the silicon oxide film is formed by surface oxidation of a silicon substrate while using the Kr/O_2 high-density plasma, provided that the silicon oxide film has a thickness of 4nm or

5 more. It can be seen that the Kr concentration in the silicon oxide film decreases toward the silicon/silicon oxide surface. According to the method of silicon oxide formation of the present invention, Kr is incorporated in the silicon oxide

10 film with a surface density of $10^{10} cm^{-2}$ or more. The result of FIG.5 is obtained on the (100) surface and also on the (111) surface.

FIG.6 shows the surface state density formed in an oxide film, wherein the result of FIG.6

15 was obtained by a low-frequency C-V measurement. The silicon oxide film of FIG.6 was formed at the substrate temperature of 400°C while using the apparatus of FIG.2. In the experiment, the oxygen partial pressure in the rare gas was set to 3% and

20 the pressure in the processing chamber was set to 1 Torr (about 133 Pa). For the sake of comparison, the surface state density of a thermal oxide film formed at 900°C in a 100% oxygen atmosphere is also represented.

25 Referring to FIG.6, it can be seen that the surface state density of the oxide film is small in both of the cases in which the oxide film is formed on the (100) surface and in which the oxide film is formed on the (111) surface as long as the oxide film

30 is formed while using the Kr gas. The value of the surface state density thus achieved is comparable with the surface state density of a thermal oxide film that is formed on the (100) surface in a dry

oxidation atmosphere at 900°C. Contrary to the foregoing, the thermal oxide film formed on the (111) surface has a surface state density larger than the foregoing surface state density by a factor of 10.

5   The mechanism of the foregoing results is thought as follows.

Viewing the silicon crystal from the side of the silicon oxide film, there appear two bonds for one silicon atom when the silicon surface is the

10   (100) surface. On the other hand, there appear one bond and three bonds alternately for one silicon atom when the silicon surface is the (111) surface. Thus, when a conventional thermal oxidation process is applied to a (111) surface, oxygen atoms quickly

15   cause bonding to all the foregoing three bonds, leaving the remaining bond behind the silicon atom. Thereby, the remaining bond may extend and form a weak bond or disconnected and form a dangling bond. When this is the case, there inevitably occurs an

20   increase of surface state density.

When the high-density plasma oxidation is conducted in the mixed gas of Kr and O_2, Kr* of the intermediate excitation state cause collision with O_2 molecules and there occurs efficient formation of

25   atomic state oxygen O*, wherein the atomic state oxygen O* thus formed easily reach the weak bond or dangling bond noted before and form a new silicon-oxygen bond. With this, it is believed that the surface states are reduced also on the (111) surface.

30   In the experiment for measuring the relationship between the oxygen partial pressure in the Kr gas used for the atmosphere during the formation of the silicon oxide film and the breakdown

voltage of the silicon insulation film thus formed, and further in the experiment for measuring the relationship between the oxygen partial pressure in the Kr gas and the surface state density in the

5   silicon oxide film thus formed, it was confirmed that a generally same result is obtained for the case in which the silicon oxide film is formed on the (100) surface and for the case in which the silicon oxide film is formed on the (111) surface, and that the

10   surface state density becomes minimum when the oxygen partial pressure in the Kr gas is set to 3%, provided that the silicon oxide film is formed by setting the pressure of the processing chamber to 1 Torr (about 133Pa). Further, the breakdown voltage of the silicon

15   oxide film becomes maximum when the oxygen partial pressure is set to about 3%. From the foregoing, it is derived that an oxygen partial pressure of 2 - 4% is preferable for conducting the oxidation process by using the Kr/O_2 mixed gas.

20   FIG.7 shows a relationship between the pressure used for forming the silicon oxide film and the breakdown voltage of the silicon oxide film thus formed. Further, FIG.7 shows the relationship between the pressure and the surface state density of the

25   silicon oxide film. In FIG.7, it should be noted that the oxygen partial pressure is set to 3%.

           Referring to FIG.7, it can be seen that the breakdown voltage of the silicon oxide film becomes maximum and the surface state density becomes minimum

30   when the pressure of about 1 Torr is used at the time of forming the oxide film. From the result of FIG.7, it is concluded that the preferable pressure of forming an oxide film by using a Kr/O_2 mixed gas

would be 800 - 1200 mTorr. The result of FIG.7 is
valid not only for the process on the (100) surface
but also for the process on the (111) surface.

In addition to the foregoing, other various
preferable characteristics were obtained for the
oxide film formed by the oxidation of silicon
substrate surface by the Kr/O_2 high-density plasma
with regard to electronic and reliability
characteristics, including the breakdown
characteristic, the leakage characteristic, the
hotcarrier resistance, and the QBD (Charge-to-
Breakdown) characteristic, which represents the
amount of electric charges that leads a silicon oxide
film to breakdown as a result of application of a
stress current, wherein the characteristics thus
obtained are comparable to those of the thermal oxide
film that is formed at 900°C

FIGS.8A and 8B show the leakage current
induced by a stress current for a silicon oxide film
thus obtained, in comparison with the case of a
conventional thermal oxide film. In FIGS.8A and 8B,
the thermal oxide film has a thickness of 3.2 nm.

Referring to FIGS.8A and 8B, it can be seen
that there occurs an increase of leakage current with
injection of electric charges into the conventional
thermal oxide film, while there occurs no such a
change of electric current in the plasma oxide film
that is formed by using the Kr/O_2 plasma, even in the
case electric charges of 100 C/cm^2 are injected. Thus,
the silicon oxide film of the present invention has a
very long lifetime and it takes a very long time for
a tunneling current to cause degradation in the oxide
film. The oxide film of the present invention is thus

most suitable for the tunneling oxide film of a flash memory device.

As noted previously, the oxide film grown by the Kr/O_2 high-density plasma has a characteristic comparable with, or superior to, the conventional high-temperature thermal oxide film formed on the (100) surface, for both of cases in which the oxide film is grown on the (100) surface and the oxide film is grown on the (111) surface, in spite of the fact that the oxide film is formed at a low temperature of 400°C. It is noted that the existence of Kr in the oxide film contributes also to this effect. More specifically, the existence of Kr in the oxide film causes relaxation of stress at the Si/SiO_2 interface and decrease of the electric charges in the film and the surface state density, leading to remarkable improvement of electric properties of the oxide film. Particularly, the existence of Kr atoms with a density of $10^{10}cm^{-2}$ as represented in FIG.5 is believed to contribute to the improvement of electric properties and reliability properties of the silicon oxide film.

[SECOND EMBODIMENT]

Next, the process of forming a nitride film at a low temperature by using high-density microwave plasma will be described.

In the formation of the nitride film, the same apparatus as the one explained with reference to FIG.2 is used, except that Ar or Kr is used for the plasma excitation gas at the time of forming the nitride film.

Thus, the vacuum vessel (processing

chamber) 101 is evacuated to a high vacuum state first, and the pressure inside the processing chamber 101 is then set to about 100 mTorr (about 13Pa) by introducing an Ar gas and a NH_3 gas via the shower

5   plate 102, and the like. Further, a disk-shaped substrate such as a silicon wafer is placed on the stage 104 as the substrate 103 and the substrate temperature is set to about 500°C. As long as the substrate temperature is in the range of 400 - 500°C,

10   almost the same results are obtained.

         Next, a microwave of 2.45 GHz is introduced into the processing chamber from the coaxial waveguide 105 via the radial line slot antenna 106 and further through the dielectric plate 107, and

15   there is induced high-density plasma in the processing chamber. It should be noted that a similar result is obtained as long as a microwave in the frequency of 900 MHz or more but not exceeding 10 GHz is used. In the illustrated example, the distance

20   between the shower plate 102 and the substrate 103 is set to 6 cm. Narrower the distance, faster the film formation rate. While the present embodiment shows the example of forming a film by using the plasma apparatus that uses the radial line slot antenna, it

25   is possible to use other method for introducing the microwave into the processing chamber.

         In the present embodiment, it should be noted that an Ar gas is used for exciting plasma. However, a similar result is obtained also when a Kr

30   gas is used. While the present embodiment uses NH_3 for the plasma process gas, it is also possible to use a mixed gas of N_2 and H_2 for this purpose.

         In the high-density plasma excited in the

mixed gas of Ar or Kr and NH_3 (or alternatively N_2
and H_2), there are formed NH* radicals efficiently by
Ar* or Kr* having an intermediate excitation state,
and the NH* radicals thus formed cause the desired

5   nitridation of the substrate surface. Conventionally,
there has been no report of direct nitridation of
silicon surface. Thus, a nitride film has been formed
by a plasma CVD process, and the like. However, the
nitride film thus formed by a conventional plasma CVD

10   process does not have the quality required for a gate
insulation film of a transistor. In the nitridation
of silicon according to the present embodiment, on
the other hand, it is possible to form a high-quality
nitride film at low temperature on any of the (100)

15   surface and the (111) surface, irrespective of the
surface orientation of the silicon substrate.

Meanwhile, it should be noted that
existence of hydrogen is an important factor when
forming a silicon nitride film. With the existence of

20   hydrogen in plasma, the dangling bonds existing in
the silicon nitride film or at the nitride film
interface are terminated in the form of Si-H bond or
N-H bond, and the problem of electron trapping within
the silicon nitride film or on the silicon nitride

25   interface is eliminated. The existence of the Si-H
bond and the N-H bond in the nitride film is
confirmed in the present invention by infrared
absorption spectroscopy or X-ray photoelectron
spectroscopy. As a result of the existence of

30   hydrogen, the hysteresis of the CV characteristic is
also eliminated. Further, it is possible to suppress
the surface state density of the silicon/silicon
nitride interface below $3 \times 10^{10} cm^{-2}$ by setting the

substrate temperature to 500°C or more. In the event
the silicon nitride film is formed by using an inert
gas (Ar or Kr) and a mixed gas of N_2/H_2, the number
of the traps of electrons or holes in the film

5   decreases sharply by setting the partial pressure of
the hydrogen gas to 0.5% or more.

FIG.9 shows the pressure dependence of the
film thickness of the silicon nitride film thus
formed according to the foregoing process. In the

10   illustrated example, the ratio of the Ar gas to the
NH_3 gas is set to 98:2 in terms of partial pressure,
and the film formation was conducted over the
duration of 30 minutes.

Referring to FIG.9, it can be seen that the

15   growth rate of the nitride film increases when the
pressure in the processing chamber 101 is reduced so
as to increase the energy given to NH_3 (or N_2/H_2) from
the inert gas (Ar or Kr). From the viewpoint of
efficiency of nitridation, it is therefore preferable

20   to use the gas pressure of 50 - 100 mTorr (about 7 -
13 Pa). Further, it is preferable to set the partial
pressure of NH_3 (or N_2/H_2) in the rare gas atmosphere
to 1 - 10%, more preferably to 2 - 6%.

It should be noted that the silicon nitride

25   film of the present embodiment has a dielectric
constant of 7.9, which is almost twice as large as
that of a silicon oxide film.

FIG.10 shows the current-voltage
characteristic of the silicon nitride film of the

30   present embodiment. It should be noted that the
result of FIG.10 is obtained for the case in which a
silicon nitride film having a thickness of 4.2 nm
(2.1 nm in terms of oxide film equivalent thickness)

is formed by using a gas mixture of $Ar/N_2/H_2$ while
setting the gas composition ratio, $Ar:N_2:H_2$, to
93:5:2 in terms of partial pressure. In FIG.10, the
result for the foregoing nitride film is compared

5   also with the case of a thermal oxide film having a
thickness of 2.1 nm.

        Referring to FIG.10, it can be seen that
there is realized a very small leakage current,
smaller than the leakage current of a silicon oxide

10   film by a factor of 10^4 or more, is obtained when a
voltage of 1V is applied for the measurement. This
result indicates that the silicon nitride film thus
obtained can be used as the insulating film that is
provided between a floating gate electrode and a

15   control gate electrode of a flash memory device for
suppressing the leakage current flowing therebetween.

        It should be noted that the foregoing
condition of film formation, the property of the film,
or the electric characteristic of the film are

20   obtained similarly on any of the surfaces of the
silicon crystal. In other words, the same result is
obtained on the (100) surface and also on the (111)
surface. According to the present invention,
therefore, it is possible to form a silicon nitride

25   film of excellent quality on any of the crystal
surfaces of silicon. It should be noted that the
existence of the Si-H bond or N-H bond in the film is
not the only cause of the foregoing advantageous
effect of the present invention. The existence of Ar

30   or Kr in the film contributes also to the foregoing
advantageous result. As a result of the existence of
Ar or Kr in the film, it should be noted that the
stress within the nitride film or the stress at the

silicon/nitride film interface is relaxed
substantially, while this relaxation of stress also
contributes to the reduction of fixed electric
charges and the surface state density in the silicon
5   nitride film, which leads to the remarkable
improvement of electric properties and reliability.
Particularly, the existence of Ar or Kr with the
density of $10^{10}cm^{-2}$ is thought as contributing
effectively to the improvement of electric
10   characteristics and reliability of the silicon
nitride film, just in the case of the silicon oxide
film represented in FIG.5.

[THIRD EMBODIMENT]

15   The foregoing method of forming oxide film
or nitride film is applicable also to the oxidation
or nitridation of polysilicon. Thus, the present
invention enables formation of a high-quality oxide
film or nitride film on polysilicon.

20   Hereinafter, the method of forming a
dielectric film on a polysilicon film according to a
third embodiment of the present invention will be
described with reference to FIGS.11A and 11B.

             Referring to FIG.11A, a polysilicon film
25   203 is deposited on a silicon substrate 201 covered
by an insulation film 202. By exposing the
polysilicon film 203 to the high-density mixed gas
plasma of Kr or Ar and oxygen in the processing
vessel 101 of the microwave plasma processing
30   apparatus of FIG.2 in the step of FIG.11B, a silicon
oxide film 204 having a high film quality is obtained
on the surface of the polysilicon film 203, wherein
the silicon oxide film 204 thus formed is

characterized by small surface state density and
small leakage current.

In the step of FIG.11B, it is also possible
to form a high-quality nitride film 205 on the
5   surface of the polysilicon film 203 by exposing the
polysilicon film 203 to the high-density mixed gas
plasma of Kr or Ar and NH_3 or N_2 and H_2.

Further, it is possible, in the step of
FIG.11B, to form a high-quality oxynitride film 206
10   on the surface of the polysilicon film 203, by
exposing the polysilicon film 203 to the high-density
mixed gas plasma of Kr or Ar and oxygen and NH_3 or N_2
and H_2.

It should be noted that a polysilicon film
15   formed on an insulation film tends to take a stable
state in which the (111) surface is oriented in the
direction perpendicular to the insulation film. The
polysilicon film having this state is dense and
provides good quality. On the other hand, crystal
20   grains of other crystal orientation may exist also in
the polysilicon film. According to the method of
forming an oxide film or a nitride film or an
oxynitride film of the present embodiment, it becomes
possible to form a high-quality oxide film, or a
25   high-quality nitride film or a high-quality
oxynitride film, irrespective of the surface
orientation of silicon layer. Thus, the process of
FIGS.11A and 11B is most suitable for forming a high
quality thin oxide film or a nitride film or an
30   oxynitride film on a polysilicon film. It should be
noted that the polysilicon film may be the first
polysilicon gate electrode that constitutes the
floating electrode of flash memory. As the oxide film

or nitride film or oxynitride film of the present
invention can be formed at a low temperature of 550°C
or less, there arises no problem of rough surface
formation on the polysilicon surface.

5   FIG.12 shows the result of the experiment
of forming an oxide film on an n-type polysilicon
film having the thickness of 200 nm, wherein it
should be noted that the polysilicon film is formed
on a thermal oxide film covering the (100) oriented
10   surface of a Si substrate with a thickness of 100 nm.
It should be noted that FIG.12 also shows the case in
which the (100) surface and the (111) surface of a Si
substrate is oxidized directly. In FIG.12, the
vertical axis represents the thickness of the oxide
15   film thus formed, while the horizontal axis
represents the duration of the process. Further, ▲
in FIG.12 shows the case in which an oxide film is
formed by processing the polysilicon surface thus
formed by the Kr/O_2 plasma, while ● in FIG.12 shows
20   the case in which an oxide film is formed by
processing the (100) surface of the Si substrate by
the Kr/O_2 plasma. Further, ■ in FIG.12 shows the case
in which an oxide film is formed by processing the
(111) surface of the Si substrate by the Kr/O_2 plasma.
25   In FIG.12, it should further be noted that ○
represents the case of causing thermal oxidation of
the (100) surface of the Si substrate, while □
represents the case of causing a thermal oxidation of
the (111) surface of the Si substrate. Further, △
30   represents the case in which thermal oxidation is
applied to the surface of a polysilicon film. It
should be noted that the Kr/O_2 plasma processing was
conducted at the temperature of 400°C, by using the

apparatus explained already with reference to FIG.2 while setting the internal pressure of the processing chamber 101 to 1 Torr (about 133 Pa) and setting the ratio of the Kr gas and the oxygen gas to 97:3 in

5 terms of flow-rate. On the other hand, the thermal oxidation process was conducted at 900°C in the 100% oxygen atmosphere. In the experiment of FIG.12, it should be noted that the polysilicon film is doped to a carrier density exceeding $10^{20} cm^{-3}$.

10 Referring to FIG.12, no substantial difference of oxidation process can be seen when the oxidation process is conducted on the (100) surface and when the oxidation process is conducted on the (111) surface, as long as the Kr/O_2 plasma process is

15 used for the oxidation process, as explained already. Further, it can be seen that substantially the same oxidation rate is achieved in the case of oxidizing the polysilicon film. Further, it should be noted that the oxidation rate thus obtained is

20 substantially identical with the oxidation rate observed when applying a thermal oxidation process to a polysilicon film. In contrast, it can be seen that, when the conventional thermal oxidation process is applied, the oxidation rate of the Si substrate

25 surface is much slower, indicating that the oxide film thus formed has a much smaller thickness.

From FIG.12, it will be understood that a nearly identical oxidation rate is achieved for a Si surface as long as the Kr/O2 plasma is used for the

30 oxidation process, irrespective of whether the Si surface is a surface of a single-crystal Si of an arbitrary orientation or a polycrystalline surface including grain boundaries.

FIG.13A shows the result of atomic-force microscopy applied to the surface of a polysilicon film thus formed before the oxidation process is conducted.

5 FIG.13B, on the other hand, shows the state of the polysilicon surface of FIG.13A after the Kr/O_2 plasma processing is conducted. In the state of FIG.13B, it should be noted that the polysilicon surface is covered by the oxide film formed as a

10 result of the Kr/O_2 plasma process. Further, FIG.13C shows the polysilicon surface in the state the oxide film is removed from the surface of FIG.13B by an HF processing.

Referring to FIGS.13A - 13C, the oxidation

15 process in the Kr/O_2 plasma is effective at low temperature as low as 400°C, and there is caused no substantial grain growth in the polysilicon film. Associated therewith, there is no problem of surface roughening in the polysilicon film. The oxide film

20 thus has a generally uniform thickness.

In contrast, FIG.14A shows the surface state of a polysilicon film subjected to thermal oxidation process at 900°C in the state that the polysilicon film carries thereon the oxide film,

25 while FIG.14B shows the surface state in which the oxide film of FIG.14A is removed.

Referring to FIGS.14A and 14B, it can be seen that there occurs a substantial crystal grain growth in the polysilicon film as a result of the

30 thermal processing, and that there has been caused a substantial roughening in the polysilicon film surface. When a thin oxide film is formed on such a rough surface, there tends to occur the problem of

concentration of electric field, while such a
concentration of the electric field causes the
problem in the leakage current characteristics and
problems in the breakdown characteristics.

5   FIGS.15A and 15B represent the result of
transmission microscopic observation showing the
cross-section of the specimen in which an oxide film
is formed on a polysilicon film surface by the Kr/O_2
plasma processing. It should be noted that FIG.15B
10   shows a part of the area of FIG.15A in an enlarged
scale.

          Referring to FIG.15A, it can be seen that
there is formed an Al layer on the oxide film
(designated as "polyoxide"), wherein FIG.15A clearly
15   shows that the oxide film thus formed has a uniform
thickness on the polysilicon film surface. Further,
the enlarged view of FIG.15B indicates that the oxide
film is uniform.

          FIG.16 shows the relationship between the
20   current density of the silicon oxide film thus formed
on the polysilicon film and the electric field
applied thereto, in comparison with a corresponding
relationship for a thermal oxide film. Further,
FIG.17 is a diagram that shows the relationship of
25   FIG.16 in the Fowler-Nordheim plot.

          Referring to FIGS.16 and 17, it can be seen
that the tunneling current starts to increase in the
case the oxide film is formed on the polysilicon film
by the Kr/O_2 plasma oxidation process when the
30   applied electric field has exceeded 5 MV/cm. Further,
the plot of FIG.17 indicates that the tunneling
current flowing through the oxide film is a Fowler-
Nordheim tunneling current, similarly to the case of

the thermal oxide film. Further, from FIG.17, it can
be seen that there appears a larger barrier height ϕ
$_B$ of tunneling in the case the oxide film is formed
by the Kr/O_2 plasma oxidation process as compared

5   with the case of the thermal oxide film. Further, it
can be seen that there is caused an increase of
breakdown voltage as compared with the case of
conventional thermal oxide film.

10   [FOURTH EMBODIMENT]

Next, the construction of a flash memory
device according to a fourth embodiment of the
present invention will be described with reference to
FIG.18, wherein the flash memory device of the

15   present embodiment uses the art of the low-
temperature oxide film formation conducted in the
microwave plasma explained before.

Referring to FIG.18, the flash memory
device is constructed on a silicon substrate 1001 and

20   includes a tunneling oxide film 1002 formed on the
silicon substrate 1001 and a first polysilicon gate
electrode 1003 formed on the tunneling oxide film
1002 as a floating gate electrode, wherein the
polysilicon gate electrode 1003 is covered by a

25   silicon oxide film 1004, and a second polysilicon
gate electrode 1008 is formed on the silicon oxide
film 1004 as a control gate electrode. In FIG.18,
illustration of source region, drain region, contact
holes, interconnection patterns, and the like is

30   omitted.

In the flash memory device of such a
construction, a high quality film characterized by
small leakage current is obtained for the oxide film

1004 as a result of the exposure of the polysilicon
gate electrode 1003 to the high-density plasma that
is formed in the microwave plasma processing
apparatus of FIG.2 by using the Kr/O$_2$ plasma gas.

5   Thus, it becomes possible to reduce the thickness of
the oxide film 1004, and low-voltage driving of the
flash memory device becomes possible.

In the flash memory device of FIG.18, it is
also possible to use a nitride film 1005 formed by

10   the Kr/NH$_3$ plasma processing as explained before in
place of the oxide film 1004. Further, it is also
possible to use an oxynitride film 1009 as explained
before with reference to the previous embodiment.

15   [FIFTH EMBODIMENT]

Next, the fabrication process of a flash
memory device according to a fifth embodiment of the
present invention will be described, wherein the
flash memory device of the present embodiment uses

20   the technology of low-temperature formation of oxide
film and nitride film while using the microwave
plasma explained above, wherein the present
embodiment also includes a high-voltage transistor
and a low-voltage transistor having a gate electrode

25   of polysilicon/silicide stacked structure.

FIG.19 shows the schematic cross-sectional
structure of a flash memory device 1000 according to
the present embodiment.

Referring to FIG.19, the flash memory

30   device 1000 is constructed on the silicon substrate
1001 and includes the tunneling oxide film 1002
formed on the silicon substrate 1001 and the first
polysilicon gate electrode 1003 formed on the

tunneling oxide film 1002 as a floating gate electrode, wherein the polysilicon gate electrode 1003 is further covered consecutively by the silicon nitride film 1004, a silicon oxide film 1005, a

5   silicon nitride film 1006 and a silicon oxide film 1007, and the second polysilicon gate electrode 1008 is formed further on the silicon nitride film 1007 as a control gate electrode. In FIG.19, illustration of source region, drain region, contact holes,

10 interconnection patterns, and the like, is omitted.

In the flash memory of the present embodiment, the silicon oxide films 1002, 1005 and 1007 are formed according to the process of silicon oxide film formation explained before. Further, the

15 silicon nitride films 1004 and 1006 are formed according to the process of silicon nitride film formation explained before. Thus, excellent electric property is guaranteed even when the thickness of these films is reduced to one-half the thickness of

20 conventional oxide film or nitride film.

Next, the fabrication process of a semiconductor integrated circuit including the flash memory device of the present embodiment will be explained with reference to FIGS.20 - 25.

25 Referring to FIG.20, a silicon substrate 1101 carries a field oxide film 1102 such that the field oxide film 1102 defines, on the silicon substrate 1101, a flash memory cell region A, a high-voltage transistor region B and a low-voltage

30 transistor region C, wherein each of the regions A - C is formed with a silicon oxide film 1103. The field oxide film 1102 may be formed by a selective oxidation (LOCOS) process or a shallow trench

isolation process.

In the present embodiment, a Kr gas is used for the plasma excitation gas at the time of formation of the oxide film and the nitride film.
Further, the microwave plasma processing apparatus of FIG.2 is used for the formation of the oxide film and the nitride film.

Next, in the step of FIG.21, the silicon oxide film 1103 is removed in the memory cell region A and a tunneling oxide film 1104 is formed on the memory cell region A with a thickness of about 5 nm. During the formation of the tunneling oxide film 1104, the vacuum vessel (reaction chamber) 101 is evacuated to a vacuum state and the Kr gas and an O_2 gas is introduced from the shower plate 102 such that the pressure inside of the reaction chamber reaches 1 Torr (about 133Pa). Further, the temperature of the silicon wafer is set to 450°C, and a microwave of 2.56 GHz frequency in the coaxial waveguide 105 is supplied to the interior of the processing chamber via the radial line slot antenna 106 and the dielectric plate 107. As a result, there is formed a high-density plasma.

In the step of FIG.21, a first polysilicon film 1105 is deposited, after the step of forming the tunneling oxide film 1104, such that the first polysilicon film 1105 covers the tunneling oxide film 1104, and the surface of the polysilicon film 1105 thus deposited is planarized by conducting a hydrogen radical processing. Further, the first polysilicon film 1105 is removed from the high-voltage transistor region B and the low-voltage transistor region by way of patterning, leaving the first polysilicon film

1105 selectively on the tunneling oxide film 1104 of the memory cell region.

Next, in the step of FIG.22, a lower nitride film 1106A, a lower oxide film 1106B, an
5 upper nitride film 1106C and an upper oxide film 1106D are formed consecutively on the structure of FIG.21. As a result, an insulation film 1106 having an NONO structure is formed by using the microwave plasma processing apparatus of FIG.2.

10 In more detail, the vacuum vessel (processing chamber) 101 of the microwave plasma processing apparatus of FIG.2 is evacuated to a high-vacuum state, and the Kr gas, an N_2 gas and an H_2 gas are introduced into the processing chamber 101 from
15 the shower plate 102 until the pressure inside the processing chamber is set to about 100 mTorr (about 13Pa). Further, the temperature of the silicon wafer is set to 500°C. In this state, a microwave of 2.45 GHz frequency is introduced into the processing
20 chamber from the coaxial waveguide 105 via the radial line slot antenna 106 and the dielectric plate 107, and there is formed a high-density plasma in the processing chamber. As a result of this, a silicon nitride film of about 6 nm thickness is formed on the
25 polysilicon surface as the lower nitride film 1106A.

Next, the supply of the microwave is interrupted. Further, the supply of the Kr gas, the N_2 gas and the H_2 gas is interrupted, and the vacuum vessel (processing chamber) 101 is evacuated.
30 Thereafter, the Kr gas and the O_2 gas are introduced again into the processing chamber via the shower plate 102, and the pressure in the processing chamber is set to 1 Torr (about 133 Pa). In this state, the

microwave of 2.45 GHz frequency is supplied again, and there is formed high-density plasma in the processing chamber 101. As a result, a silicon oxide film of about 2 nm thickness is formed as the lower

5   oxide film 1106B.

Next, the supply of the microwave is again interrupted. Further, the supply of the Kr gas and the O_2 gas is interrupted, and the processing chamber 101 is evacuated. Thereafter, the Kr gas, the N_2 gas

10   and the H_2 gas are introduced into the processing chamber via the shower plate 102 so that the pressure inside the processing chamber is set to 100 mTorr (about 13Pa). In this state, a microwave of 2.45 GHz frequency is introduced and high-density plasma is

15   formed in the processing chamber 101. As a result of the plasma processing using the high-density plasma thus formed, there is further formed a silicon nitride film of 3 nm thickness.

Finally, the supply of the microwave is

20   interrupted. Further, the supply of the Kr gas, the N_2 gas and the H_2 gas is also interrupted, and the vacuum vessel (processing chamber) 101 is evacuated. Thereafter, the Kr gas and the O_2 gas are introduced again via the shower plate 102 and the pressure

25   inside the processing chamber is set to 1 Torr (about 133 Pa). In this state, the microwave of 2.45 GHz frequency is again supplied, and high-density plasma is formed in the processing chamber 101. As a result, a silicon oxide film of 2 nm thickness is formed as

30   the upper oxide film 1106D.

Thus, according to the foregoing process steps, it becomes possible to form the insulation film 1106 of the NONO structure with a thickness of 9

nm. It was confirmed that the NONO film 1106 thus formed does not depends on the surface orientation of polysilicon and that each of the oxide films and the nitride films therein is highly uniform in terms of

5   film thickness and film quality.

In the step of FIG.22, the insulation film 1106 thus formed is further subjected to a patterning process such that the insulation film 1106 is selectively removed in the high-voltage transistor

10 region B and in the low-voltage transistor region C.

Next, in the step of FIG.23, an ion implantation process is conducted into the high-voltage transistor region B and further into the low-voltage transistor region C for the purpose of

15 threshold control. Thereafter, the oxide film 1103 is removed from the foregoing regions B and C, and a gate oxide film 1107 is formed on the high-voltage transistor region B with a thickness of 7 nm, followed by the formation of a gate oxide film 1108

20 on the low-voltage transistor region C with a thickness of 3.5 nm.

In the step of FIG.23, the overall structure including the field oxide film 1102 is covered consecutively with a second polysilicon film

25 1109 and a silicide film 1110. By patterning the polysilicon film 1109 and the silicide film 1110, a gate electrode 111B is formed in the high-voltage transistor region B and a gate electrode 111C is formed in the low-voltage transistor region C.

30 Further, the polysilicon film 1109 and the silicide film 110 are patterned in the memory cell region, and a gate electrode 1111A is formed.

Finally, a standard semiconductor process

including formation of source and drain regions, formation of insulation films, formation of contact holes and formation of interconnections, is conducted, and the semiconductor device is completed.

It should be noted that the silicon oxide film and the silicon nitride film in the NONO film 1101 thus formed shows excellent electric properties in spite of the fact that the each of the silicon oxide and silicon nitride films therein has a very small thickness. Further, the silicon oxide film and the silicon nitride film are dense and have a feature of high film quality. As the silicon oxide film and the silicon nitride film are formed at low temperature, there occurs no problem of thermal budget formation, and the like, at the interface between the gate polysilicon and the oxide film, and an excellent interface is obtained.

In the flash memory integrated circuit device in which the flash memory devices of the present invention are arranged in a two-dimensional array, it becomes possible to carry out writing and erasing of information at low voltage. Further, the semiconductor integrated circuit has advantageous features of suppressing substrate current and suppressing degradation of the tunneling insulation film. Thus, the semiconductor integrated circuit has a reliable device characteristic. The flash memory device of the present invention is characterized by a low leakage current, and enables writing of information at a voltage of about 7 V. Further, the flash memory device of the present invention can retain the written information over a duration longer than a conventional flash memory device by a factor

of 10. The number of times the rewriting can be made is increased also by a factor of 10 in the case of the flash memory of the present invention over a conventional flash memory device.

[SIXTH EMBODIMENT]

Next, a flash memory device according to a second embodiment of the present invention will be described, wherein the flash memory device of the present embodiment has a gate electrode having a polysilicon/silicide stacked structure and is formed by using the art of low-temperature formation of oxide and nitride film that uses the high-density microwave plasma explained before.

FIG.24 shows a schematic cross-sectional structure of a flash memory device 1500 according to the present embodiment.

Referring to FIG.24, the flash memory device 1500 is constructed on a silicon substrate 1501 and includes a tunneling nitride film 1502 formed on the silicon substrate 1501 and a first polysilicon gate electrode 1503 formed on the tunneling nitride film 1502 as a floating gate electrode, wherein the first polysilicon gate electrode 1503 is covered consecutively by a silicon oxide film 1504, a silicon nitride film 1505 and a silicon oxide film 1506. Further, a second polysilicon electrode 1507 forming a control gate electrode is formed on the silicon oxide film 1506. In FIG.24, illustration of source region, drain region, contact holes, interconnection patterns, and the like, is omitted.

In the flash memory device 1500 of FIG.24,

the silicon oxide films 1502, 1504 and 1506 are
formed according to a process of forming a silicon
oxide film that uses the high-density microwave
plasma explained before. Further, the silicon nitride
5   film 1505 is formed by a process of forming a silicon
nitride film that uses the high-density microwave
plasma explained before.

In the present embodiment, too, the process
steps up to the step of patterning the first
10   polysilicon film 1503 are identical with those of the
steps of FIGS.20 and 21, except for the point that
the tunneling nitride film 1502 is formed after the
step of evacuating the vacuum vessel (processing
chamber) 101, by introducing an Ar gas, an N_2 gas and
15   an H_2 gas from the shower plate 102 such that the
pressure inside the processing chamber becomes 100
mTorr (about 13Pa). Thereby, the tunneling nitride
film 1502 is formed to have a thickness of about 4 nm,
by supplying a microwave of 2.45 GHz to form high-
20   density plasma in the processing chamber.

After the first polysilicon film 1503 is
thus formed, the lower silicon oxide film 1504 and
the silicon nitride film 1505 and the upper silicon
oxide film 1506 are formed consecutively on the first
25   polysilicon film, and an insulation film having an
ONO structure is obtained.

In more detail, the vacuum chamber
(processing chamber) 101 of the microwave plasma
processing apparatus explained previously with
30   reference to FIG.2 is evacuated to a high vacuum
state, and the Kr gas and an O_2 gas are introduced
into the processing chamber via the shower plate 102
such that the pressure of the processing chamber 101

is set to 1 Torr (about 133 Pa). In this state, the microwave of 2.45 GHz is supplied to the processing chamber 101 and there is formed the high-density plasma therein. As a result, a silicon oxide film

5   having a thickness of about 2 nm is formed on the surface of the first polysilicon film 1503.

Next, a silicon nitride film is formed on the silicon oxide film by a CVD process with a thickness of 3 nm, and the vacuum vessel (processing

10   chamber) 101 is evacuated. Further, the Ar gas, the N_2 gas and the H_2 gas are introduced into the processing chamber via the shower plate 102, and the pressure inside the processing chamber is set to 1 Torr (about 133 Pa). In this state, the microwave of

15   2.45 GHz is supplied again and the high-density plasma is formed in the processing chamber 101. By exposing the foregoing silicon nitride film to the hydrogen nitride radicals NH* formed with the high-density plasma, the silicon nitride film is converted

20   to a dense silicon nitride film.

Next, a silicon oxide film is formed on the foregoing dense silicon nitride film by a CVD process with a thickness of about 2 nm, and the pressure of the processing chamber 101 of the microwave plasma

25   processing apparatus is set to 1 Torr (about 133 Pa) by supplying thereto the Kr gas and the O_2 gas. By supplying the microwave of 2.45 GHz further to the processing chamber in this state, the high-density plasma is formed in the processing chamber 101.

30   Thereby, the CVD oxide film formed previously in the CVD process is converted to a dense silicon oxide film by exposing to the atomic state oxygen O* formed with the high-density plasma.

Thus, an ONO film is formed on the polysilicon film 1503 with a thickness of about 7 nm. The ONO film thus formed shows no dependence of property thereon on the orientation of the

5 polysilicon surface on which the ONO film is formed and has an extremely uniform thickness. The ONO film thus formed is then subjected to a patterning process for removing a part thereof corresponding to the high-voltage transistor region B and the low-voltage

10 transistor region C. By further applying the process steps similar to those used in the fourth embodiment before, the device fabrication process is completed.

The flash memory device thus formed has an excellent leakage characteristic characterized by low

15 leakage current, and writing and reading operation can be conducted at the voltage of about 6V. Further, the flash memory device provides a memory retention time larger by the factor of 10 over the conventional flash memory devices, similarly to the flash memory

20 device 1000 of the previous embodiment. Further, it is possible to achieve the number of rewriting operations larger by the factor of 10 over the conventional flash memory devices.

25 [SEVENTH EMBODIMENT]

Next, a description will be made on a flash memory device 1600 according to a seventh embodiment of the present invention, wherein the flash memory device 1600 has a gate electrode of

30 polysilicon/silicide stacked structure and is formed by the process that uses the microwave high-density plasma for forming low temperature oxide and nitride films.

FIG.25 shows the schematic cross-sectional structure of the flash memory device 1600.

Referring to FIG.25, the flash memory device 1600 is constructed on a silicon substrate 1601 and includes a tunneling oxide film 1602 formed on the silicon substrate 1061 and a first polysilicon gate electrode 1603 formed on the tunneling oxide film 1602, wherein the first polysilicon gate electrode 1603 is covered consecutively by a silicon nitride film 1604 and a silicon oxide film 1605. Further, a second polysilicon gate electrode 1606 is formed on the silicon oxide film 1605 as a control gate electrode.

In FIG.25, illustration of source region, drain region, contact holes, and interconnection patterns, is omitted.

In the flash memory 1600 of FIG.25, the silicon oxide films 1602 and 1605 are formed by the film forming process of oxide film explained above, while the silicon nitride film 1604 is formed by the film forming process of nitride film also explained above.

Next, the fabrication process of a flash memory integrated circuit according to the present invention will be explained.

In the present embodiment, too, the process proceeds similarly to the previous embodiments up to the step of patterning the first polysilicon film 1603, and the first polysilicon film 1603 is formed in the region A. Thereafter, an insulation film having an NO structure is formed by consecutively depositing a silicon nitride film and a silicOon oxide film on the first polysilicon film 1603.

In more detail, the NO film is formed by using the microwave plasma processing apparatus of FIG.2 according to the process steps noted below.

First, the vacuum vessel (processing chamber) 101 is evacuated, and a Kr gas, an N2 gas and an H2 gas are introduced thereto via the shower plate 102 and the pressure inside the processing chamber is set to about 100 mTorr (about 13Pa). In this state, a microwave of 2.45 GHz is supplied, and high-density plasma is induced in the processing chamber. Thereby, there occurs a nitriding reaction in the polysilicon film 1603 and a silicon nitride film is formed with a thickness of about 3 nm.

Next, a silicon oxide film is formed by a CVD process to a thickness of about 2 nm, and a Kr gas and an O2 gas are introduced in the microwave plasma processing apparatus such that the pressure inside the processing chamber is set to about 1 Torr (about 133Pa). In this sate, a microwave of 2.45 GHz frequency is supplied to form high-density plasma in the processing chamber, such that the oxide film formed by the CVD process is exposed to the atomic state oxygen O* associated with the high-density plasma. As a result, the CVD oxide film is converted to a dense silicon oxide film.

The NO film is thus formed to a thickness of about 5 nm, wherein the NO film thus formed has an extremely uniform thickness irrespective of the surface orientation of the polysilicon crystals. The NO film thus formed is then subjected to a patterning process and the part thereof covering the high-voltage transistor region B and the low-voltage transistor region C are removed selectively.

After the foregoing process, the process steps similar to those of FIG.23 are conducted and the device fabrication process is completed.

It should be noted that the flash memory

5   device thus formed has a low leakage characteristic, and enables writing or erasing at a low voltage as low as 5 V. Further, the flash memory device provides a memory retention time larger than the conventional memory retention time by a factor of 10, and

10   rewriting cycles larger than the conventional rewriting cycles by a factor of 10.

It should be noted that the fabrication process of the memory cell, the high-voltage transistor and the low-voltage transistor merely

15   represents an example, and the present invention is by no means limited to these embodiments. For example, it is possible to use an Ar gas in place of the Kr gas during the formation process of the nitride film. Further, it is possible to use a film having a

20   stacked structure of polysilicon/silicide/polysilicon/refractory metal/amorphous silicon or polysilicon, for the first and second polysilicon films.

Further, it is also possible to use another

25   plasma processing apparatus in place of the microwave plasma processing apparatus of FIG.2 for forming the oxide film or nitride film of the present invention, as long as the plasma processing apparatus enables low temperature formation of an oxide film. Further,

30   the radial line slot antenna is not the only solution for introducing a microwave into the processing chamber of the plasma processing apparatus, and the microwave may be introduced by other means.

In place of the microwave plasma processing apparatus of FIG.2, it is also possible to use a plasma processing apparatus having a two-stage shower plate construction, in which the plasma gas such as the Kr gas or Ar gas is introduced from a first shower plate and the processing gas is introduced from a second shower plate different from the first shower plate. In this case, it is also possible to introduce the oxygen gas from the second shower plate. Further, it is possible to design the process such that the floating gate electrode of the flash memory device and the gate electrode of the high-voltage transistor are formed simultaneously by the first polysilicon electrode.

Further, the present invention is not limited to the embodiments described heretofore, but various variations and modifications may be made without departing from the scope of the invention.

INDUSTRIAL APPLICABILITY

According to the present invention, it becomes possible to form a high-quality silicon oxide film, silicon nitride film or silicon oxynitride film on a polysilicon film with excellent characteristics and reliability comparable with, or superior to, those of a silicon thermal oxide film formed at a high temperature of about 1000°C or a CVD silicon nitride film, by using a Kr-containing insulation film formed by a novel plasma oxidation process or nitridation process conducted at a low temperature lower than 550°C. Thus, the present invention realizes a high quality and high-performance flash memory device, which allows rewriting operation at

low voltage and provides excellent electric charge
retention characteristic.